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(71) Applicant: CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US).

(72) Inventor: PRICE, Michael, W.; 32 Park Lane, Big Flats, NY 14814 (US).

(74) Agent: MURPHY, Edward F; Corning Incorporated, SP TI 3 1, Corning, NY 14831 (US).

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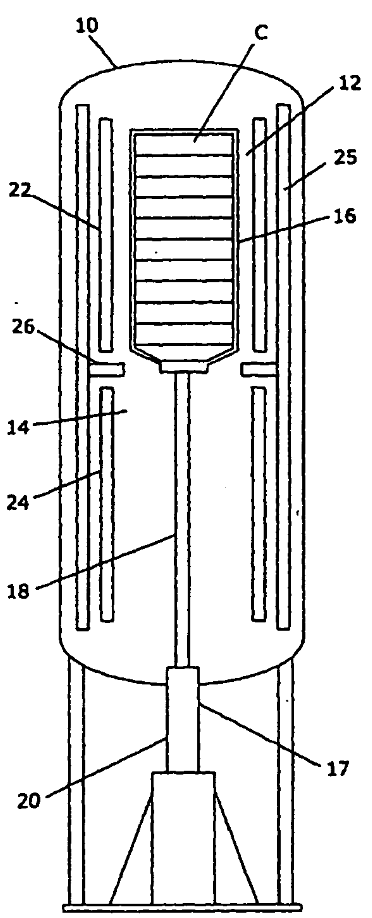
(54) Title: METHOD AND DEVICE FOR PRODUCING OPTICAL FLUORIDE CRYSTALS



(57) Abstract: A method for producing below 200nm transmitting optical fluoride crystals includes loading a fluoride raw material into a vertical stack having at least 6 crystal growth chambers, heating the vertical stack to a temperature sufficient to maintain the fluoride raw material in a molten condition, applying a crystal growth thermal gradient to the vertical stack to form optical fluoride crystals within the molten fluoride raw material, and cooling the crystals.

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METHOD AND DEVICE FOR PRODUCING OPTICAL FLUORIDE CRYSTALS

Cross Reference to Related Applications

[0001] This application claims priority from U.S. Provisional Application 60/240,304, entitled "Device/Method for Producing Optical Fluoride CaF_2 Crystals," filed October 13, 2000.

Background of Invention

[0002] Optical fluoride crystals are useful materials because of their low-wavelength absorption edges. Optical fluoride crystals such as CaF_2, BaF_2, SrF_2, LiF, MgF_2, and NaF are useful in applications that require high transmission in the vacuum ultraviolet (VUV) region, *i.e.*, at wavelengths below 200 nm. Optical fluoride crystals are particularly useful as below 200nm transmitting optical element preforms for formation into optical elements with below 200nm transmission, such as VUV microlithography optical elements (lens, prisims).Optical fluoride crystals are commonly directionally solidified by the Bridgman-Stockbarger technique. Other techniques for growing optical fluoride crystals include the Gradient Freeze technique and the Traveling Heater technique.

[0003] The Bridgman-Stockbarger technique is illustrated in Figures 1A and 1B. In Figure 1A, a crucible **C** containing a fluoride raw material **F** is disposed inside a hot zone **HZ** of a vertical furnace **1**. Heaters **2** are provided to heat the hot zone **HZ** to a temperature sufficient to melt the fluoride raw material **F**. After melting the fluoride raw material **F**, the crucible **C** is slowly lowered from the hot zone **HZ** to a cold zone **CZ**, as shown in Figure 1B. The cold zone **CZ** is at a temperature lower than the melting point of the fluoride raw material **F**. As the crucible **C** passes from the hot zone **HZ** to the cold zone **CZ**, the molten material **MF** goes through a zone having a thermal gradient designed to grow a good crystal (crystal growth thermal gradient) . On passing through this zone, the temperature transition inside the molten material **MF** creates a crystal front **CF**. The crystal growth front **CF** propagates inside the

crucible **C**, within the molten material **MF**, as long as the crucible **C** is caused to move downwardly.

[0004] The Gradient Freeze technique is illustrated in Figures 2A and 2B. In Figure 2A, a crucible **C** containing a fluoride raw material **F** is disposed inside a vertical furnace **3**. The vertical furnace **3** is provided with two heaters **4** for creating an axial crystal growth thermal gradient within the crucible **C**. A single heater that is capable of creating a crystal growth thermal gradient across the axial axis of the crucible **C** may also be used. The vertical furnace **3** is heated to a temperature sufficient to melt the fluoride raw material **F**. After melting the fluoride raw material **F**, the power applied to the heaters **4** is decreased in a manner that allows a desired axial crystal growth thermal gradient within the crucible **C** to be sustained. As shown in Figure 2B, as the power applied to the heaters **4** is decreased, the molten fluoride material **MF** is directionally solidified into a solid fluoride material **SF**.

[0005] The Traveling Heater method is illustrated in Figures 3A and 3B. In Figure 3A, a crucible **C** containing a fluoride raw material **F** is disposed inside a vertical furnace **5**. The furnace **5** includes three heaters **6** for creating a desired axial thermal profile within the furnace. Alternatively, two heaters capable of creating a desired axial thermal profile within the furnace may be used. The crucible **C** is initially located in the upper section of the vertical furnace **5** and heated to a temperature less than the melting point of the fluoride raw material **F**. As shown in Figure 3B, the crucible **C** is then moved into the middle zone of the furnace **5** that is at a temperature above the melting point of the fluoride raw material. At this position, a portion of the fluoride raw material is melted. As the crucible **C** moves relative to the furnace, the molten raw material **MF** re-solidifies into "good" material **SF**. The melted raw material **MF** moves continually inside the crucible **C** until all the material inside the crucible **C** has been re-solidified.

[0006] Typically, crystals are produced one at a time in either a net size or a large size that is machined to a desired shape. In either case, productivity is low and production cost is high. The number of crystals produced per furnace run, which require minimal machining, can be increased by loading one or more stacks of crucibles within the furnace, where each crucible contains a fluoride raw material. Multiple crystals can then be produced per furnace run using any of the techniques described above.

However, using vertically-stacked crucibles does not automatically improve productivity. Productivity can still be hampered by dead times for loading the furnace, evacuating the furnace, heating the different thermal zones of the furnace, cooling the different thermal zones of the furnace, and unloading the furnace. Also, production costs can prove prohibitive if too many crystals are grown in a single furnace run. Up till now, selection of the number of crystals to produce per furnace run has been arbitrary.

Summary of Invention

[0007] In one aspect, the invention relates to a method for producing optical fluoride crystals which comprises loading a fluoride raw material into a vertical stack having at least 6 crystal growth chambers, heating the vertical stack to a temperature sufficient to maintain the fluoride raw material in a molten condition, applying a crystal growth thermal gradient to the vertical stack to form crystals within the molten fluoride raw material, and cooling the crystals.

[0008] In another aspect, the invention relates to a method for producing optical fluoride crystals which comprises loading a fluoride raw material into multiple vertical stacks, wherein at least one vertical stack has at least 6 crystal growth chambers. The method further includes heating the vertical stacks to a temperature sufficient to maintain the fluoride raw material in a molten condition, applying a crystal growth thermal gradient to the vertical stacks to form crystals within the molten fluoride raw material, and cooling the crystals.

[0009] In another aspect, the invention relates to a device for growing optical fluoride crystals which comprises a furnace having a capacity to hold a vertical stack having at least 6 crystal growth chambers and at least one heating element to maintain an appropriate treatment temperature inside the furnace.

[0010] Other features and advantages of the invention will be apparent from the following description and the appended claims.

Brief Description of Drawings

[0011] Figures 1A and 1B illustrate a process for forming a crystal using the Bridgman-Stockbarger technique.

[0012] Figures 2A and 2B illustrate a process for forming a crystal using the Gradient Freeze technique.

[0013] Figures 3A and 3B illustrates a process for forming a crystal using the Traveling Heater technique.

[0014] Figure 4 shows a plot of normalized output as a function of stack size.

[0015] Figure 5 shows a plot of percent increase in output as a function of stack size.

[0016] Figure 6 shows a plot of capital investment as a function of stack size for various anticipated yields.

[0017] Figure 7 shows a device for producing crystals according to an embodiment of the invention.

[0018] Figure 8 shows multiple vertical stacks of crucibles arranged in a melting chamber of a furnace.

[0019] Figures 9A-9C show alternate furnace configurations.

Detailed Description

[0020] Embodiments of the invention provide a device and a method for producing crystals using one or more vertical stacks of crystal growth chambers. Specific embodiments of the invention are described below. In the following detailed description of the invention, numerous specific details are set forth in order to provide a more thorough understanding of the invention. However, it will be apparent to one of ordinary skill in the art that the invention may be practiced without these specific details. In other instances, well-known features have not been described in detail to avoid obscuring the invention.

[0021] The underlying driver in the production of crystals is how fast the crystals can be delivered to the customer. If multiple crystals can be produced in a single furnace run, then it would be possible to deliver more crystals to the customer within a given

time frame. Of course, the crystals have to be good crystals. A "good crystal" may be defined as one that meets the specifications of the target application. As an example, a fluoride crystal for use in microlithography applications may be required to meet the following specifications: (1) greater than 40% of the volume of the crystal should consist of one grain of the fluoride material, (2) the refractive index of the crystal should not vary by more than 4 ppm across a flat surface of the crystal when measured using a 632-nm laser, (3) the average birefringence of the crystal should be less than 4 nm/cm when measured using a 632-nm laser, (4) the initial internal transmission of the crystal should be greater than 99.0% at wavelengths greater than 155 nm and greater than 75.0% at wavelengths between 135 nm and 155 nm, and (5) the crystal should have a diameter in a range from 40 to 400 mm and a thickness in a range from 10 to 300 mm.

[0022] In the invention, multiple crystals are grown in vertically stacked crucibles or crystal growth chambers. The process of growing multiple crystals can be divided into a solidification segment and an annealing segment. During solidification, molten raw material is translated through a crystal growth thermal gradient to form a crystal. The solidification time is a function of the stack height and the rate at which the stack is translated. The solidification time is given by the following expression:

$$t_s = \frac{nh}{v} \tag{1}$$

where t_s is the solidification time, n is the number of crucibles in the stack, h is the height of each crucible in the stack, and v is the translation rate of the stack. The annealing step involves slowly cooling the crystals in the stack and is assumed to be independent of the stack height. The total time for a single furnace run can then be estimated as follows:

$$T = t_s + t_a \tag{2}$$

where T is the total time for a furnace run, t_s is the solidification time from equation (1) above, and t_a is the annealing time.

[0023] Table 1 shows the number of days required to run a single furnace as a function of the number of crystals produced by the furnace in a single run. Table 1 also shows the number of furnace runs and the total number of crystals that can be

made in a year. The data shown in Table 1 is based on the following assumptions: (1) each new crystal adds 100 mm to the height of the stack, (2) the translation rate of the stack is 2.5 mm/hr, and (3) the annealing time is 17 days. It should be noted that these assumptions are presented for illustration purposes only and are not intended to limit the invention. For example, the thickness of the crystals may be in a range from 10 to 300 mm, the translation rate may be in a range from 0.5 mm/hr to 5 mm/hr, and the annealing time may be in a range from 2 to 30 days. The trends shown in Table 1 and in other tables and figures that will be discussed below hold true for these ranges.

[0024] Table 1 shows that the number of days required to run a furnace increases as the number of crystals produced in a single run of the furnace increases. Table 1 also shows that the total number of crystals that can be produced in a single year increases as the number of crystals produced per furnace run increases.

Table 1: Crystal Production Data For a One-Year Period

Stack Size	No. of Days per Furnace Run	No. of Runs per Year	No. of Crystals per Year
2	20.3	18.0	35.9
3	22.0	16.6	49.8
4	23.7	15.4	61.7
5	25.3	14.4	72.0
6	27.0	13.5	81.1
7	28.7	12.7	89.1
8	30.3	12.0	96.3
9	32.0	11.4	102.7
10	33.7	10.8	108.4
11	35.3	10.3	113.6
12	37.0	9.9	118.4
13	38.7	9.4	122.7
14	40.3	9.0	126.7
15	42.0	8.7	130.4
16	43.7	8.4	133.7
17	45.3	8.1	136.9
18	47.0	7.8	139.8
19	48.7	7.5	142.5
20	50.3	7.3	145.0
21	52.0	7.0	147.4
22	53.7	6.8	149.6
23	55.3	6.6	151.7
24	57.0	6.4	153.7
25	58.7	6.2	155.5
26	60.3	6.0	157.3
27	62.0	5.9	159.0
28	63.7	5.7	160.5

Stack Size	No. of Days per Furnace Run	No. of Runs per Year	No. of Crystals per Year
29	65.3	5.6	162.0
30	67.0	5.4	163.4
31	68.7	5.3	164.8
32	70.3	5.2	166.1
33	72.0	5.1	167.3
34	73.7	5.0	168.5
35	75.3	4.8	169.6
36	77.0	4.7	170.6
37	78.7	4.6	171.7
38	80.3	4.5	172.7
39	82.0	4.5	173.6
40	83.7	4.4	174.5
41	85.3	4.3	175.4
42	87.0	4.2	176.2
43	88.7	4.1	177.0
44	90.3	4.0	177.8
45	92.0	4.0	178.5

[0025] The data shown in Table 1 does not account for downtime. Table 2 shows the data of Table 1 adjusted for downtime. The assumptions made in Table 2 are that there are 2 idle days between furnace runs and that every seventh furnace run is aborted because of furnace failure. Thus, the data in Table 2 gives a more conservative estimate of the number of furnace runs that can be made per year and the number of crystals that can be produced per year.

Table 2: Crystal Production Data For a One-Year Period Including Downtime

Stack Size	No. of Operating Days per Year	No. of Runs per Year	No. of Crystals per Year
2	279.0	13.7	27.4
3	281.7	12.8	38.4
4	284.0	12.0	48.0
5	286.0	11.3	56.5
6	287.8	10.7	64.0
7	289.4	10.1	70.7
8	290.8	9.6	76.7
9	292.0	9.1	82.1
10	293.2	8.7	87.1
11	294.2	8.3	91.6
12	295.1	8.0	95.7
13	296.0	7.7	99.5
14	296.8	7.4	103.0
15	297.5	7.1	106.2
16	298.1	6.8	109.2

Stack Size	No. of Operating Days per Year	No. of Runs per Year	No. of Crystals per Year
17	298.8	6.6	112.0
18	299.3	6.4	114.6
19	299.9	6.2	117.1
20	300.4	6.0	119.3
21	300.8	5.8	121.5
22	301.3	5.6	123.5
23	301.7	5.5	125.4
24	302.1	5.3	127.2
25	302.4	5.2	128.9
26	302.8	5.0	130.5
27	303.1	4.9	132.0
28	303.4	4.8	133.4
29	303.7	4.6	134.8
30	304.0	4.5	136.1
31	304.2	4.4	137.3
32	304.5	4.3	138.5
33	304.7	4.2	139.7
34	304.9	4.1	140.7
35	305.2	4.1	141.8
36	305.4	4.0	142.8
37	305.6	3.9	143.7
38	305.8	3.8	144.6
39	306.0	3.7	145.5
40	306.1	3.7	146.4
41	306.3	3.6	147.2
42	306.5	3.5	147.9
43	306.6	3.5	148.7
44	306.8	3.4	149.4
45	306.9	3.3	150.1

[0026] Table 3 expands the data of Table 2 to a five year period. Specifically, Table 3 shows the number of operating days, the number of furnace runs in 5 years, and the number of crystals produced in 5 years for stack size ranging from 2 to 45. Table 3 also shows normalized outputs, where the normalized outputs are obtained by dividing the number of crystals produced within the 5-year period for each stack size by the number of crystals produced within the 5-year period for a stack size of 45. Figure 4 shows a plot of normalized output as a function of stack size. If normalized output is used as an indicator of production efficiency, then Figure 4 shows that production efficiency increases as the stack size increases.

[0027] Also shown in Table 3 is the percent increase in output as the number of crystals produced in a single furnace increases. Figure 5 shows percent increase in output plotted as a function of stack size. As can be observed from the figure, output

increases as stack size increases, but at a diminishing rate. The greatest gain in output occurs in going from 2 crystals per furnace run to 3 crystals per furnace run. Increase in output rapidly diminishes from 40% to 13.3% as stack size increases from 3 to 6. Increase in output continues to diminish, but at a slower rate, from 13.3% to 1.9% as stack size increases from 6 to 20. Beyond a stack size of 20, the increase in output is fairly constant and less than 1.9%.

Table 3: Crystal Production Data for Five-Year Period Including Downtime

Stack Size	No. of Operating Days in 5 Years	No. of Furnace Runs in 5 Years	No. of Crystals in 5 Years	Normalized Output	Percent Increase in Output
2	1394.8	68.6	137.2	0.2	0.0
3	1408.4	64.0	192.1	0.3	40.0
4	1420.1	60.0	240.0	0.3	25.0
5	1430.2	56.5	282.3	0.4	17.6
6	1439.1	53.3	319.8	0.4	13.3
7	1447.0	50.5	353.3	0.5	10.5
8	1454.0	47.9	383.5	0.5	8.5
9	1460.2	45.6	410.7	0.5	7.1
10	1465.9	43.5	435.4	0.6	6.0
11	1471.0	41.6	457.9	0.6	5.2
12	1475.6	39.9	478.6	0.6	4.5
13	1479.9	38.3	497.5	0.7	4.0
14	1483.8	36.8	515.0	0.7	3.5
15	1487.4	35.4	531.2	0.7	3.1
16	1490.7	34.1	546.2	0.7	2.8
17	1493.8	33.0	560.2	0.7	2.6
18	1496.6	31.8	573.2	0.8	2.3
19	1499.3	30.8	585.3	0.8	2.1
20	1501.8	29.8	596.7	0.8	1.9
21	1504.1	28.9	607.4	0.8	1.8
22	1506.3	28.1	617.5	0.8	1.7
23	1508.3	27.3	627.0	0.8	1.5
24	1510.3	26.5	635.9	0.8	1.4
25	1512.1	25.8	644.3	0.9	1.3
26	1513.8	25.1	652.4	0.9	1.2
27	1515.4	24.4	659.9	0.9	1.2
28	1517.0	23.8	667.1	0.9	1.1
29	1518.4	23.2	674.0	0.9	1.0
30	1519.8	22.7	680.5	0.9	1.0
31	1521.1	22.2	686.7	0.9	0.9
32	1522.4	21.6	692.7	0.9	0.9
33	1523.6	21.2	698.3	0.9	0.8
34	1524.7	20.7	703.7	0.9	0.8
35	1525.8	20.3	708.9	0.9	0.7
36	1526.9	19.8	713.9	1.0	0.7

Stack Size	No. of Operating Days in 5 Years	No. of Furnace Runs in 5 Years	No. of Crystals in 5 Years	Normalized Output	Percent Increase in Output
37	1527.9	19.4	718.6	1.0	0.7
38	1528.9	19.0	723.2	1.0	0.6
39	1529.8	18.7	727.6	1.0	0.6
40	1530.7	18.3	731.8	1.0	0.6
41	1531.5	17.9	735.8	1.0	0.6
42	1532.3	17.6	739.7	1.0	0.5
43	1533.1	17.3	743.5	1.0	0.5
44	1533.9	17.0	747.1	1.0	0.5
45	1534.6	16.7	750.6	1.0	0.5

[0028] Another factor to consider in production of crystals is cost. The initial capital investment for the furnaces and the cost of running the furnaces determine the cost of the crystals and whether it is economically feasible to produce a certain number of crystals in a single furnace run. In general, the number of furnaces required to produced a certain number of good crystals decreases as the stack size increases and depends on the yield of the furnace. Table 4 shows the number of good crystals produced per furnace over a 5 year period for various anticipated yield values.

Table 4: Number of Good Crystals Produced Over a Five-Year Period for Various Anticipated Yield Values

Stack Size	1%	5%	10%	20%	50%	80%
2	1	6	13	27	68	109
3	1	9	19	38	96	153
4	2	12	24	48	120	192
5	2	14	28	56	141	225
6	3	15	31	63	159	255
7	3	17	35	70	176	282
8	3	19	38	76	191	306
9	4	20	41	82	205	328
10	4	21	43	87	217	348
11	4	22	45	91	228	366
12	4	23	47	95	239	382
13	4	24	49	99	248	398
14	5	25	51	103	257	412
15	5	26	53	106	265	424
16	5	27	54	109	273	436
17	5	28	56	112	280	448
18	5	28	57	114	286	458
19	5	29	58	117	292	468
20	5	29	59	119	298	477

Stack Size	1%	5%	10%	20%	50%	80%
21	6	30	60	121	303	485
22	6	30	61	123	308	493
23	6	31	62	125	313	501
24	6	31	63	127	317	508
25	6	32	64	128	322	515
26	6	32	65	130	326	521
27	6	32	65	131	329	527
28	6	33	66	133	333	533
29	6	33	67	134	336	539
30	6	34	68	136	340	544
31	6	34	68	137	343	549
32	6	34	69	138	346	554
33	6	34	69	139	349	558
34	7	35	70	140	351	562
35	7	35	70	141	354	567
36	7	35	71	142	356	571
37	7	35	71	143	359	574
38	7	36	72	144	361	578
39	7	36	72	145	363	582
40	7	36	73	146	365	585
41	7	36	73	147	367	588
42	7	36	73	147	369	591
43	7	37	74	148	371	594
44	7	37	74	149	373	597
45	7	37	75	150	375	600

[0029] Table 5 shows the number of furnaces required to produce 300 good crystals over a 5 year period for various anticipated yield values. The data shows that the number of furnaces required to produce the crystals decreases as the stack size increases.

Table 5: Number of Furnaces Required to Produce 300 Good Crystals for Various Anticipated Yield Values

Stack Size	1%	5%	10%	20%	50%	80%
2	300	50	23	11	4	3
3	300	33	16	8	3	2
4	150	25	13	6	3	2
5	150	21	11	5	2	1
6	100	20	10	5	2	1
7	100	18	9	4	2	1
8	100	16	8	4	2	1
9	75	15	7	4	1	1
10	75	14	7	3	1	1
11	75	14	7	3	1	1
12	75	13	6	3	1	1

Stack Size	1%	5%	10%	20%	50%	80%
13	75	13	6	3	1	1
14	60	12	6	3	1	1
15	60	12	6	3	1	1
16	60	11	6	3	1	1
17	60	11	5	3	1	1
18	60	11	5	3	1	1
19	60	10	5	3	1	1
20	60	10	5	3	1	1
21	50	10	5	2	1	1
22	50	10	5	2	1	1
23	50	10	5	2	1	1
24	50	10	5	2	1	1
25	50	9	5	2	1	1
26	50	9	5	2	1	1
27	50	9	5	2	1	1
28	50	9	5	2	1	1
29	50	9	4	2	1	1
30	50	9	4	2	1	1
31	50	9	4	2	1	1
32	50	9	4	2	1	1
33	50	9	4	2	1	1
34	43	9	4	2	1	1
35	43	9	4	2	1	1
36	43	9	4	2	1	1
37	43	9	4	2	1	1
38	43	8	4	2	1	1
39	43	8	4	2	1	1
40	43	8	4	2	1	1
41	43	8	4	2	1	1
42	43	8	4	2	1	1
43	43	8	4	2	1	1
44	43	8	4	2	1	1
45	43	8	4	2	1	1

[0030] Table 6 shows estimated capital costs in dollars for furnaces based on production of 300 good crystals for different stack sizes and anticipated yield values of the furnaces. The data in Table 6 is based on the assumptions that the base cost of a furnace that produces two crystals in a single furnace run is $500,000 and that each additional crystal produced by the furnace in a single furnace run will increase the cost of the furnace by $20,000. In general, the base cost of the furnace may range from $200,000 to $1,000,000 and each additional crystal may increase the cost of the furnace by $5,000 to $50,000. The trends shown in Table 6 hold true regardless of the actual dollar estimates used for the furnaces. Figure 6 shows capital investment as a function of stack size for various anticipated yields. As shown in Figure 6, capital

investment cost initially decreases as the stack size increases and then starts to increase again around a stack size of 26.

Table 6: Furnace Cost Based on Production of 300 Good Crystals for Various Anticipated Yield Values

Stack Size	1%	5%	10%	20%	50%	80%
2	150,000,000	25,000,000	11,538,462	5,555,556	2,205,882	1,376,147
3	156,000,000	17,333,333	8,210,526	4,105,263	1,625,000	1,019,608
4	84,000,000	14,000,000	7,000,000	3,500,000	1,400,000	875,000
5	87,000,000	12,428,571	6,214,286	3,107,143	1,234,043	773,333
6	60,000,000	12,000,000	5,806,452	2,857,143	1,132,075	705,882
7	62,000,000	10,941,176	5,314,286	2,657,143	1,056,818	659,574
8	64,000,000	10,105,263	5,052,632	2,526,316	1,005,236	627,451
9	49,500,000	9,900,000	4,829,268	2,414,634	965,854	603,659
10	51,000,000	9,714,286	4,744,186	2,344,828	940,092	586,207
11	52,500,000	9,545,455	4,666,667	2,307,692	921,053	573,770
12	54,000,000	9,391,304	4,595,745	2,273,684	903,766	565,445
13	55,500,000	9,250,000	4,530,612	2,242,424	895,161	557,789
14	45,600,000	9,120,000	4,470,588	2,213,592	887,160	553,398
15	46,800,000	9,000,000	4,415,094	2,207,547	883,019	551,887
16	48,000,000	8,888,889	4,444,444	2,201,835	879,121	550,459
17	49,200,000	8,785,714	4,392,857	2,196,429	878,571	549,107
18	50,400,000	9,000,000	4,421,053	2,210,526	881,119	550,218
19	51,600,000	8,896,552	4,448,276	2,205,128	883,562	551,282
20	52,800,000	9,103,448	4,474,576	2,218,487	885,906	553,459
21	45,000,000	9,000,000	4,500,000	2,231,405	891,089	556,701
22	46,000,000	9,200,000	4,524,590	2,243,902	896,104	559,838
23	47,000,000	9,096,774	4,548,387	2,256,000	900,958	562,874
24	48,000,000	9,290,323	4,571,429	2,267,717	908,517	566,929
25	49,000,000	9,187,500	4,593,750	2,296,875	913,043	570,874
26	50,000,000	9,375,000	4,615,385	2,307,692	920,245	575,816
27	51,000,000	9,562,500	4,707,692	2,335,878	930,091	580,645
28	51,000,000	9,272,727	4,636,364	2,300,752	918,919	574,109
29	52,000,000	9,454,545	4,656,716	2,328,358	928,571	578,850
30	53,000,000	9,352,941	4,676,471	2,338,235	935,294	584,559
31	54,000,000	9,529,412	4,764,706	2,364,964	944,606	590,164
32	55,000,000	9,705,882	4,782,609	2,391,304	953,757	595,668
33	56,000,000	9,882,353	4,869,565	2,417,266	962,751	602,151
34	48,857,143	9,771,429	4,885,714	2,442,857	974,359	608,541
35	49,714,286	9,942,857	4,971,429	2,468,085	983,051	613,757
36	50,571,429	10,114,286	4,985,915	2,492,958	994,382	619,965
37	51,428,571	10,285,714	5,070,423	2,517,483	1,002,786	627,178
38	52,285,714	10,166,667	5,083,333	2,541,667	1,013,850	633,218
39	53,142,857	10,333,333	5,166,667	2,565,517	1,024,793	639,175
40	54,000,000	10,500,000	5,178,082	2,589,041	1,035,616	646,154
41	54,857,143	10,666,667	5,260,274	2,612,245	1,046,322	653,061
42	55,714,286	10,833,333	5,342,466	2,653,061	1,056,911	659,898
43	56,571,429	10,702,703	5,351,351	2,675,676	1,067,385	666,667

Stack Size	1%	5%	10%	20%	50%	80%
44	57,428,571	10,864,865	5,432,432	2,697,987	1,077,748	673,367
45	58,285,714	11,027,027	5,440,000	2,720,000	1,088,000	680,000

[0031] Table 7 shows the relative power consumption per furnace run for different stack sizes. Table 7 also shows normalized power consumption for various anticipated yields for stack size ranging from 2 to 45. The power consumption shown in Table 7 is for producing 300 disks in a 5-year period. From Table 7, it can be observed that the amount of power needed to manufacture the crystals increases dramatically as the stack size increases.

Table 7: Power Consumption for 300 Good Crystals for Various Anticipated Yield Values

Stack Size	Relative Power Consumption per Furnace Run	1%	5%	10%	20%	50%	80%
2	1.0	0.029	0.026	0.024	0.023	0.023	0.023
3	3.0	0.081	0.048	0.046	0.046	0.045	0.046
4	6.0	0.076	0.067	0.068	0.068	0.068	0.068
5	10.0	0.120	0.090	0.092	0.092	0.091	0.091
6	15.0	0.113	0.119	0.117	0.115	0.114	0.114
7	21.0	0.150	0.140	0.138	0.138	0.137	0.137
8	28.0	0.190	0.158	0.160	0.160	0.160	0.159
9	36.0	0.174	0.184	0.182	0.182	0.182	0.182
10	45.0	0.208	0.209	0.207	0.205	0.205	0.205
11	55.0	0.243	0.233	0.231	0.229	0.228	0.227
12	66.0	0.279	0.256	0.254	0.252	0.250	0.250
13	78.0	0.316	0.279	0.277	0.274	0.273	0.273
14	91.0	0.284	0.300	0.298	0.295	0.296	0.295
15	105.0	0.315	0.320	0.319	0.319	0.319	0.319
16	120.0	0.347	0.340	0.345	0.341	0.341	0.341
17	136.0	0.380	0.359	0.363	0.363	0.363	0.363
18	153.0	0.413	0.390	0.388	0.388	0.387	0.386
19	171.0	0.447	0.407	0.413	0.409	0.410	0.409
20	190.0	0.481	0.438	0.436	0.433	0.432	0.432
21	210.0	0.429	0.454	0.460	0.456	0.455	0.455
22	231.0	0.458	0.484	0.483	0.479	0.478	0.478
23	253.0	0.487	0.498	0.505	0.501	0.500	0.500
24	276.0	0.517	0.529	0.527	0.523	0.524	0.523
25	300.0	0.546	0.541	0.549	0.549	0.545	0.546
26	325.0	0.576	0.571	0.570	0.570	0.568	0.569
27	351.0	0.606	0.601	0.599	0.595	0.592	0.591

Stack Size	Relative Power Consumption per Furnace Run	1%	5%	10%	20%	50%	80%
28	378.0	0.636	0.611	0.620	0.615	0.614	0.614
29	406.0	0.667	0.641	0.640	0.640	0.638	0.636
30	435.0	0.697	0.650	0.659	0.659	0.659	0.659
31	465.0	0.728	0.679	0.688	0.683	0.682	0.682
32	496.0	0.758	0.707	0.707	0.707	0.705	0.704
33	528.0	0.789	0.736	0.735	0.730	0.727	0.728
34	561.0	0.703	0.743	0.753	0.753	0.751	0.751
35	595.0	0.730	0.771	0.782	0.776	0.773	0.772
36	630.0	0.757	0.800	0.799	0.799	0.797	0.795
37	666.0	0.783	0.828	0.827	0.822	0.818	0.819
38	703.0	0.810	0.833	0.844	0.844	0.842	0.841
39	741.0	0.837	0.860	0.872	0.866	0.865	0.863
40	780.0	0.864	0.888	0.888	0.888	0.888	0.886
41	820.0	0.891	0.916	0.916	0.909	0.911	0.909
42	861.0	0.918	0.944	0.943	0.937	0.933	0.932
43	903.0	0.945	0.945	0.958	0.958	0.956	0.955
44	946.0	0.973	0.973	0.986	0.979	0.978	0.978
45	990.0	1	1	1	1	1	1

[0032] Table 3 suggests that the higher the stack size the higher the output. However, output does not increase by much as the number of crystals produced per furnace run exceeds 20. Table 6 suggests that capital investment generally decreases as stack size increases. However, there are technological difficulties in building furnaces that can accommodate very tall stacks. Such technological difficulties include, but are not limited to, how to maintain vacuum in the furnace, how to maintain appropriate temperatures in the different thermal zones in the furnace, and how to design the crucibles to prevent leaks from hydrostatic forces. Therefore, it is important to minimize stack size while maximizing output. Table 7 suggests that power consumption increases significantly as stack size increases. Therefore, it is important to strike a balance between stack size and power consumption. In general, using a stack size in a range from 6 to 20 is productive because it provides a good balance between output and power consumption. The capital investment for this range is also minimal. Using a stack size in a range from 6 to 10 is also productive, and some of the technological difficulties associated with building very tall furnaces can be avoided.

[0033] Figure 7 shows a furnace **10** according to an embodiment of the invention. The furnace **10** includes a melting chamber **12** and an annealing chamber **14**. Inside the melting chamber **12** is a stack of crucibles **16**. In the illustration, the melting chamber **12** and annealing chamber **14** are built such that they can accommodate one or more vertically-stacked crucibles or crystal growth chambers. Figure 8 shows a possible arrangement of multiple vertically-stacked crucibles **16a, 16b, 16c** inside the melting chamber **12**. The crucibles may have the same or different diameters. Returning to Figure 7, the melting chamber **12** and annealing chamber **14** are built such that up to 10 crucibles can be stacked vertically inside them. In general, the melting and annealing chambers **12, 14** can be built to accommodate crucibles in a range from 6 to 20.

[0034] A lift mechanism **17** is coupled to the stack of crucibles **16** to lower the stack of crucibles **16** from the melting chamber **12** into the annealing chamber **14**. For example, the lift mechanism **17** could be a rod **18** coupled to a hydraulic or pneumatic actuator **20**. The actuator **20** may be controlled as necessary to translate the stack of crucibles **16** inside the furnace **10**. The melting chamber **12** and the annealing chamber **14** have associated heating elements **22, 24** for maintaining an appropriate treatment temperature inside them. Insulating material **25** is provided around the heating elements **22, 24** to contain heat in the furnace **10**. A temperature gradient between the melting chamber **12** and the annealing chamber **14** is obtained by a diaphragm **26** which partially isolates the melting chamber **12** from the annealing chamber **14**. It should be noted that the heating element **24** in the annealing chamber **14** is optional. Also, the heating element **24** does not have to extend across the entire length of the annealing chamber **14**, *i.e.*, a short heater can be used in the annealing chamber **14**, just below the diaphragm **26**.

[0035] Alternate configurations of the furnace **10** are possible. Figure 9A shows an alternate arrangement wherein a heater **28** is provided above the stack of crucibles **16**. Above the heater **28** is an insulating material **30**. The heater **32** in the annealing chamber **14** is a short heater and does not extend across the entire length of the annealing chamber **14**. Figure 9B shows another arrangement wherein heaters **34, 36** are positioned at the top and bottom of the stack **16**, respectively. The purpose of the heaters **34, 36** at the top and bottom of the stack (also heater **28** in Figure 9A) is to

provide uniform temperature distribution across the stack **16**. This has the effect of reducing thermally-induced stresses in the crystals, which would otherwise result in high birefringence values. Figure 9C shows a furnace configuration having three thermal zones **38, 40, 42**. Heaters **44, 46, 48** are positioned in the three zones **38, 40, 42**, respectively, to provide the appropriate treatment temperatures. This furnace configuration may be used to grow crystals using the previously described Traveling Heater technique. In general, the size of the furnaces can be selected such that they can accommodate one or more vertical stacks of crystal growth chambers or crucibles, where the number of crystal growth chambers in each stack may be in a range from 6 to 20.

[0036] Returning to Figure 7, the furnace **10** is hermetically sealed and the required atmosphere is created inside the melting chamber **12**, *i.e.*, vacuum, inert, or fluorinating environment. Each crucible **C** in the stack **16** contains a crystal raw material. The melting chamber **12** is heated to a temperature sufficient to melt the crystal raw material or maintain the crystal raw material in a molten state. The crucibles **C** with the molten material are slowly translated from the melting chamber **12** to the annealing chamber **14**, which is maintained at a temperature lower than the temperature in the melting chamber **12**. The crystal forms in the molten material as the molten material is translated through the temperature gradient. The length of time required to solidify the molten material depends on the stack height. The higher the stack, the longer it takes to translate the stack of crucibles from the melting chamber to the annealing chamber. The time required to cool the crystals is generally independent of the stack height.

[0037] The invention provides one or more advantages. The invention provides an optimum range of crystal growth chambers to stack together vertically in order to achieve a high production efficiency in a crystal growth batch process. The high production efficiency is achieved while maximizing output and minimizing production cost. Multiple vertical stacks of crystal growth chambers can be used in a single furnace run to further increase the output of the furnace without affecting production efficiency. The verticle stacks of the inventive methods have at least six crystal growth chambers, preferably at least seven crystal growth chambers, and more preferably at least eight crystal growth chambers. In preferred embodiments, the

methods of the invention utilize verticle stacks with six to eleven crystal growth chambers, six to ten crystal growth chambers, seven to eleven crystal growth chambers, and seven to ten crystal growth chambers. In preferred embodiments, the methods of the invention utilize fluidly interconnected crystal growth chambers to provide for crystal growth orientation transfer from one growth chamber to the next, preferably with the crystal growth orientation being a seeded crystal growth orientation with crystal orientation initiated with a seed crystal of the desired orientation such as 111 or 001.

[0038] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

What is claimed is:

[c1] A method for producing a plurality of below 200nm transmitting optical element preform optical fluoride crystals for formation into optical elements with below 200nm transmission, comprising:

loading a fluoride raw material into a vertical stack having at least 6 crystal growth chambers;

heating the vertical stack to a temperature sufficient to maintain the fluoride raw material in a molten condition;

applying a crystal growth thermal gradient to the vertical stack to grow crystals fromthe molten fluoride raw material inside said crystal growth chambers; and

cooling the plurality of grown crystals to provide below 200nm transmitting optical element preform fluoride crystals.

[c2] The method of claim 1, wherein heating the vertical stack comprises positioning the vertical stack in a first zone of a furnace and heating the first zone of the furnace to the temperature sufficient to maintain the fluoride raw material in the molten condition.

[c3] The method of claim 2, wherein applying the crystal growth thermal gradient to the vertical stack to form crystals comprises translating the vertical stack from the first zone of the furnace to a second zone of the furnace that is maintained at a temperature lower than the temperature of the first zone of the furnace.

[c4] The method of claim 1, wherein translating the vertical stack comprises translating the vertical stack at a speed of 0.5 mm/hr to 5 mm/hr.

[c5] The method of claim 1, wherein cooling the crystals comprises slowly cooling the crystals to ambient temperature for 2 to 30 days.

[c6] The method of claim 1, wherein a diameter of the crystals ranges from 10 to 300 mm.

[c7] The method of claim 1, wherein a thickness of the crystals ranges from 40 to 400 mm.

[c8] The method of claim 1, wherein a refractive index of at least one of the crystals varies by less than 4 ppm across a flat surface of the crystal when measured using a 632-nm laser.

[c9] The method of claim 1, wherein an average birefringence of at least one of the crystals is less than 4 nm/cm when measuring using a 632-nm laser.

[c10] The method of claim 1, wherein an initial internal transmission of at least one of the crystals is greater than 99% at wavelengths greater than 155 nm and greater than 75% at wavelengths between 135 nm and 155 nm.

[c11] The method of claim 1, wherein applying the thermal gradient to the vertical stack to form crystals comprises decreasing the temperature of the vertical stack in a manner that allows a desired thermal gradient to be sustained within the crystal growth chambers.

[c12] The method of claim 1, wherein the crystal growth chambers in the vertical stack range from 6 to 10.

[c13] The method of claim 1, wherein the crystal growth chambers in the vertical stack range from 6 to 20.

[c14] A method for producing optical fluoride crystals, comprising:

loading a fluoride raw material into multiple vertical stacks of crystal growth chambers, wherein at least one vertical stack has at least 6 crystal growth chambers;

heating the vertical stacks to a temperature sufficient to maintain the fluoride raw material in a molten condition;

applying a thermal gradient to the vertical stacks to form crystals within the molten fluoride raw material; and

cooling the crystals.

[c15] The method of claim 14, wherein heating the vertical stacks comprises positioning the vertical stacks in a first zone of a furnace and heating the first zone of the furnace to the temperature sufficient to maintain the fluoride raw material in the molten condition.

[c16] The method of claim **15**, wherein applying the thermal gradient to the vertical stacks to form crystals comprises translating the vertical stacks from the first zone of the furnace to a second zone of the furnace that is maintained at a temperature lower than the temperature of the first zone of the furnace.

[c17] The method of claim **14**, wherein translating the vertical stacks comprises translating the vertical stacks at a speed of 0.5 mm/hr to 5 mm/hr.

[c18] The method of claim **14**, wherein cooling the crystals comprises slowly cooling the crystals to ambient temperature for 2 to 30 days.

[c19] The method of claim **14**, wherein applying the thermal gradient to the vertical stacks to form crystals comprises decreasing the temperature of the vertical stacks in a manner that allows a desired thermal gradient to be sustained within the crystal growth chambers.

[c20] The method of claim **14**, wherein the crystal growth chambers in the vertical stacks range from 6 to 10.

[c21] The method of claim **14**, wherein the crystal growth chambers in the vertical stacks range from 6 to 20.

[c22] A device for growing optical fluoride crystals, comprising:

a furnace having a capacity to hold a vertical stack having at least 6 crystal growth chambers; and

at least one heating element to maintain an appropriate treatment temperature inside the furnace.

[c23] The device of claim **22**, wherein the crystal growth chambers in the vertical stack range from 6 to 20.

[c24] The device of claim **22**, wherein the furnace comprises a first zone and a second zone.

[c25] The device of claim **24**, further comprising a mechanism for translating the stack of crystal growth chambers from the first zone to the second zone.

[c26] The device of claim **24**, further comprising a heating element positioned at a top end of the first zone.

[c27] The device of claim **24**, further comprising a heating element positioned at a bottom end of the first zone.

[c28] The device of claim **24**, wherein the at least one heating element is disposed in the first zone.

[c29] The device of claim **28**, further comprising a heating element disposed in the second zone.

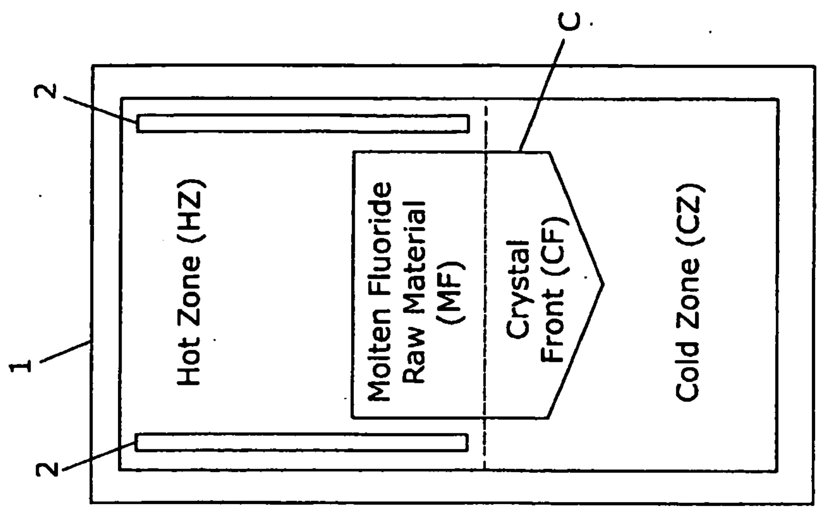

FIGURE 1B

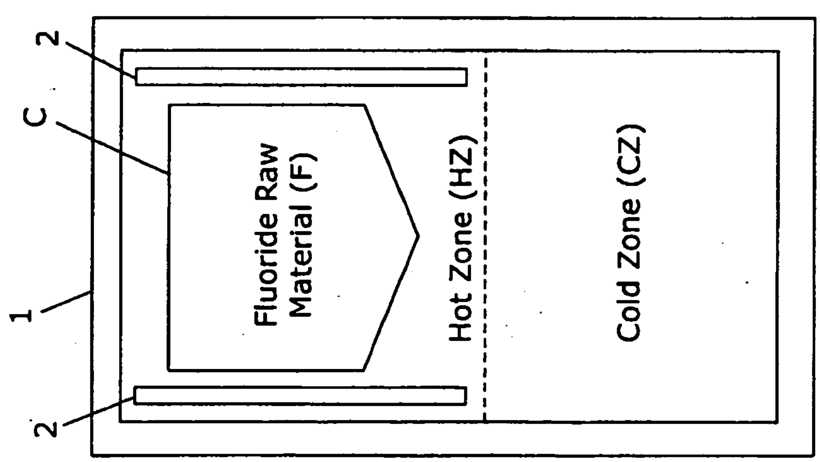

FIGURE 1A

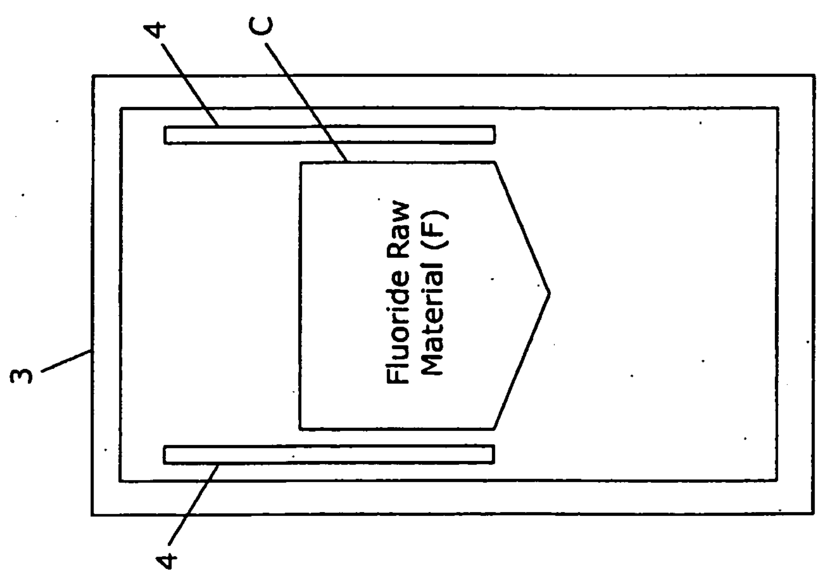

FIGURE 2A

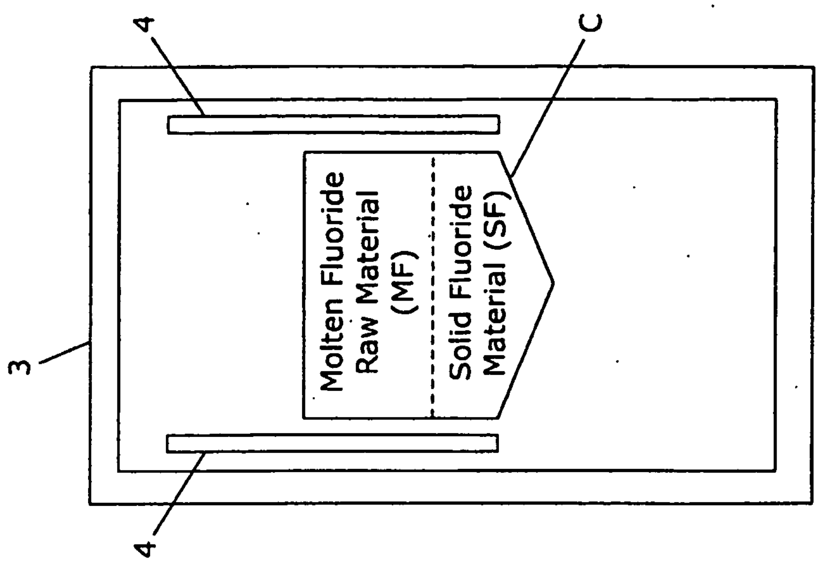

FIGURE 2B

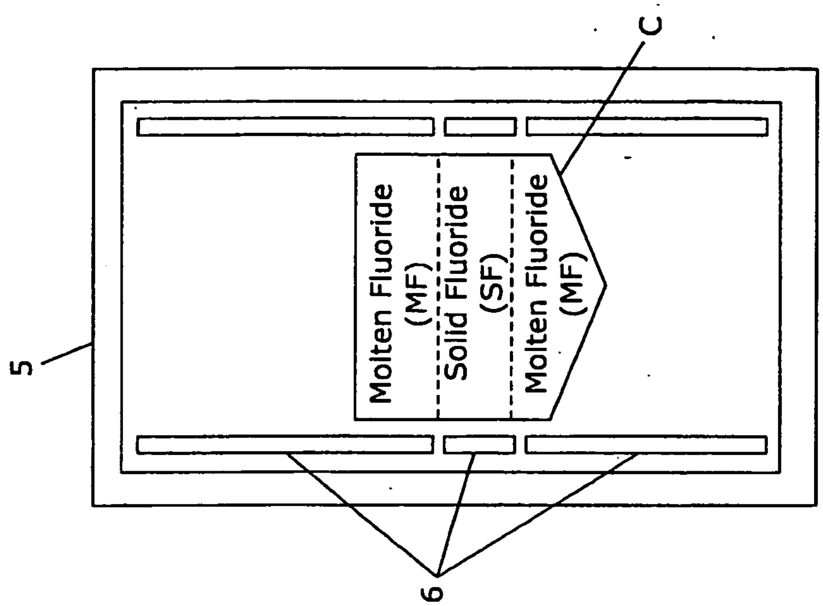

FIGURE 3B

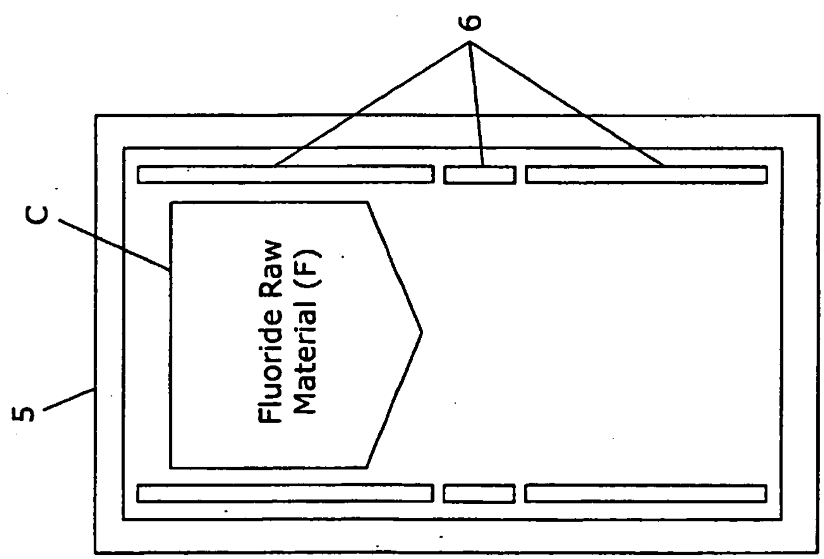

FIGURE 3A

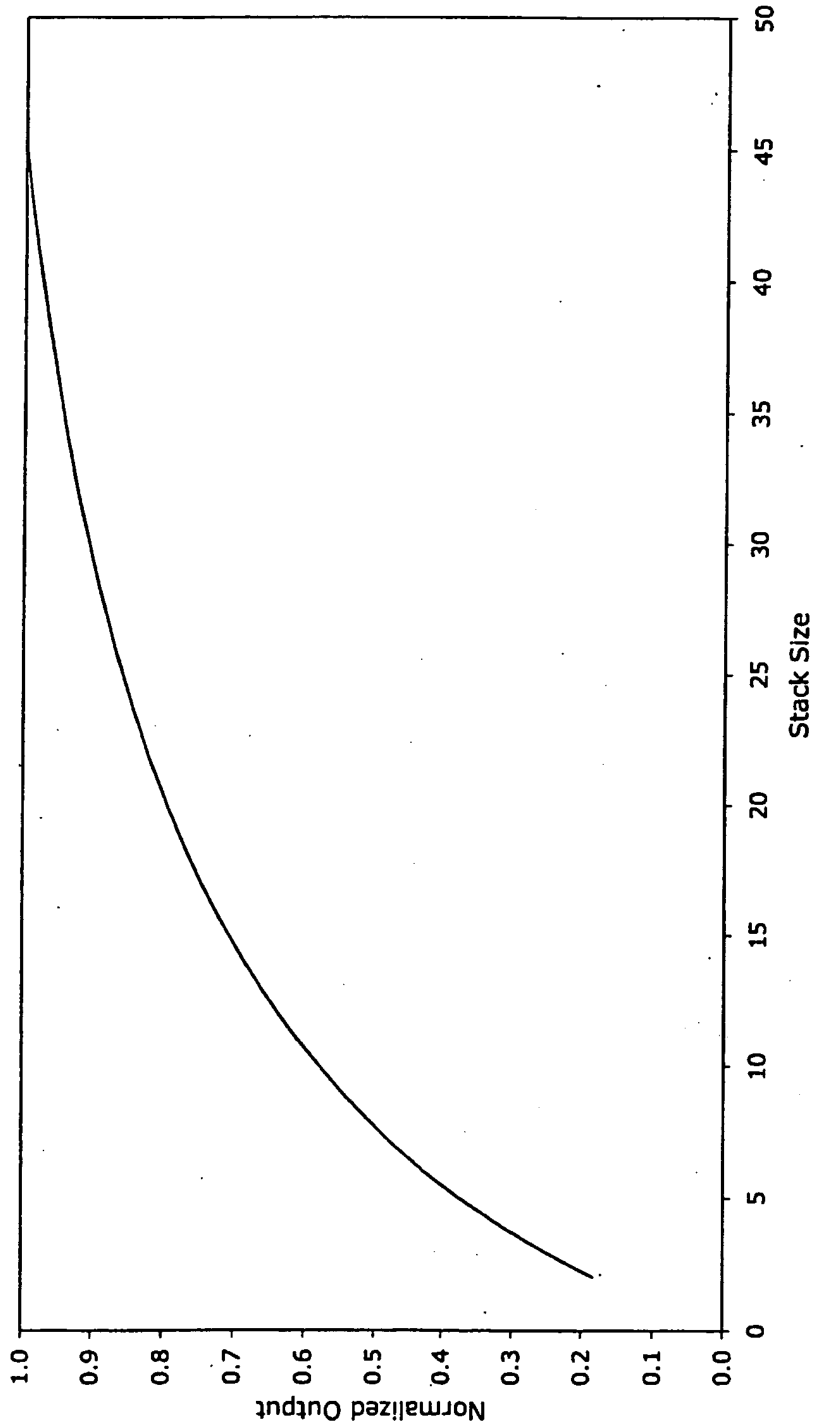
Normalized Output
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Stack Size
0
5
10
15
20
25
30
35
40
45
50

FIGURE 4

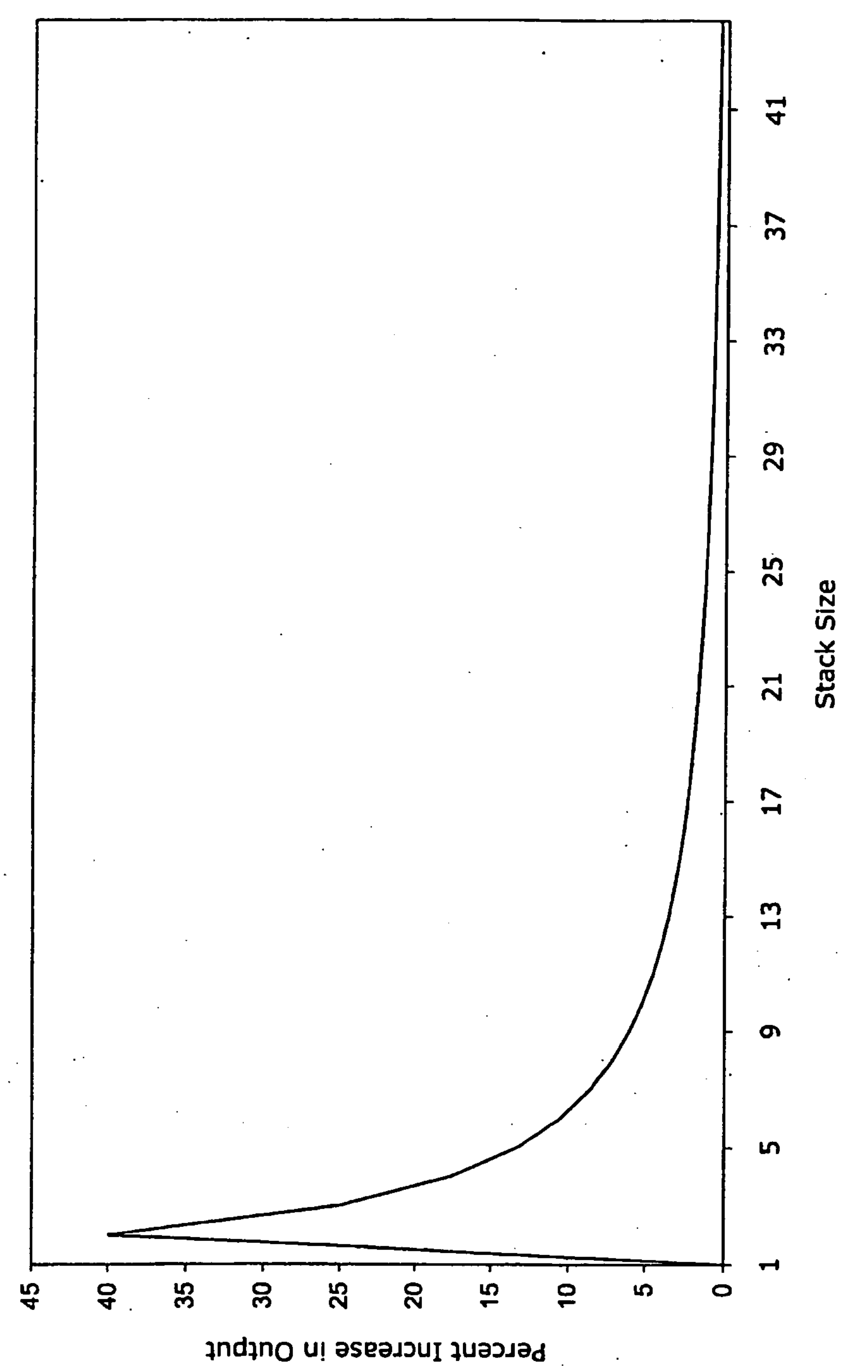
Percent Increase in Output
45
40
35
30
25
20
15
10
5
0
1
5
9
13
17
21
25
29
33
37
41
Stack Size

FIGURE 5

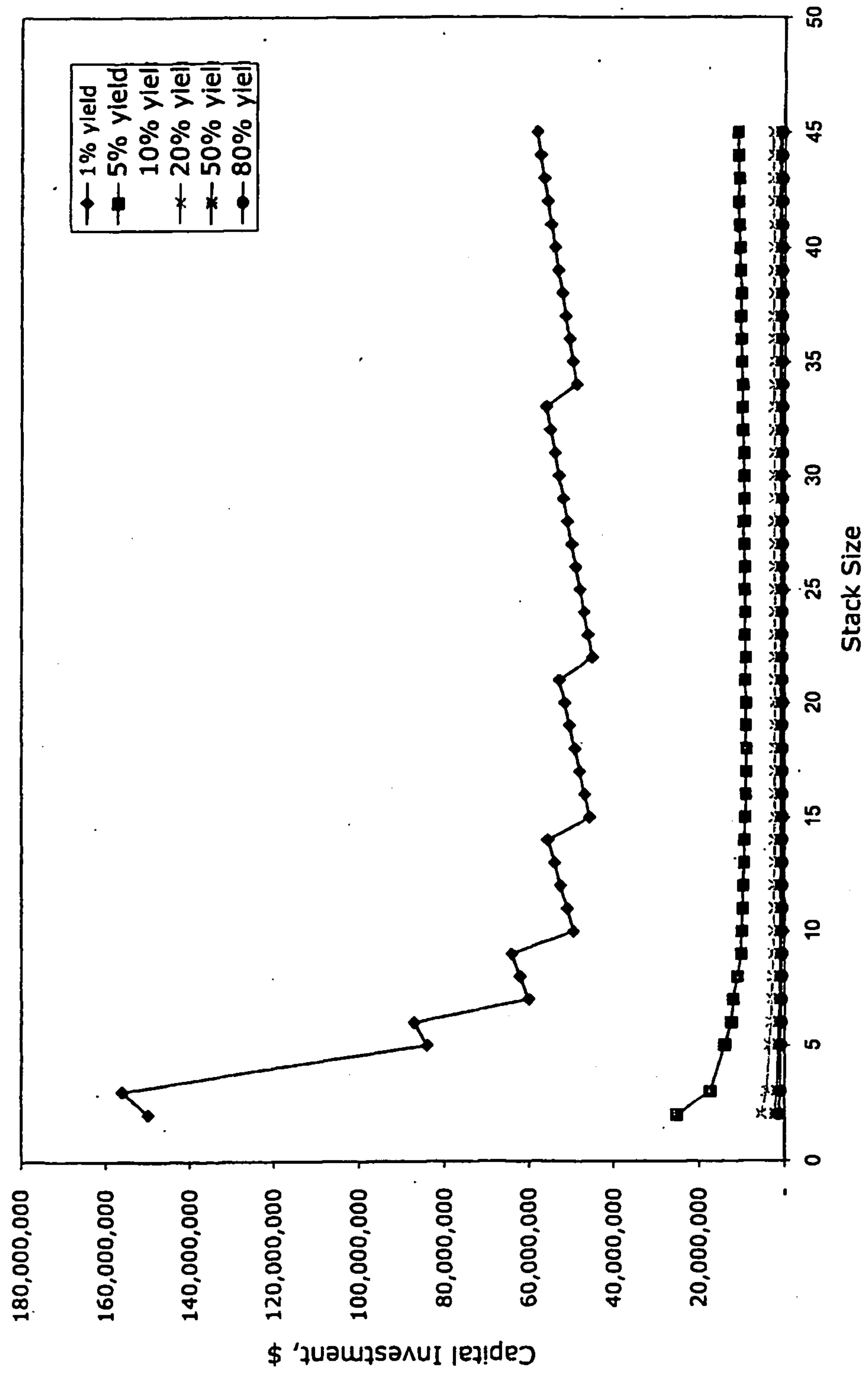
Capital Investment, $
Stack Size
1% yield
5% yield
10% yiel
20% yiel
50% yiel
80% yiel
180,000,000
160,000,000
140,000,000
120,000,000
100,000,000
80,000,000
60,000,000
40,000,000
20,000,000
-
0
5
10
15
20
25
30
35
40
45
50

FIGURE 6

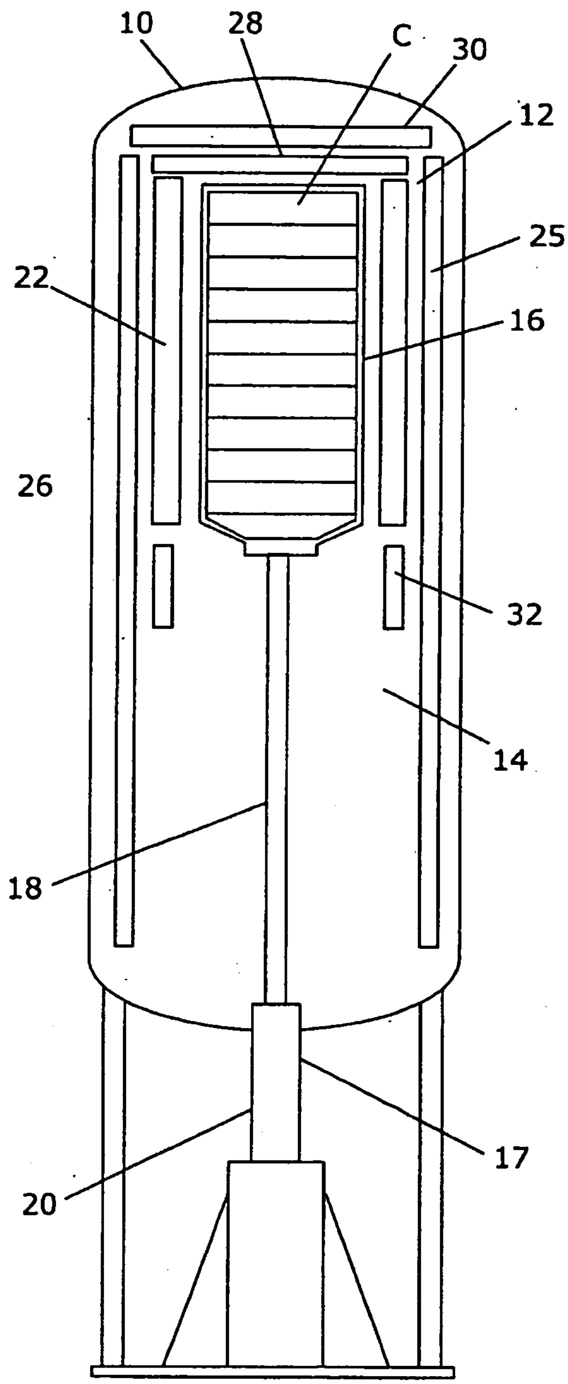

FIGURE 9A

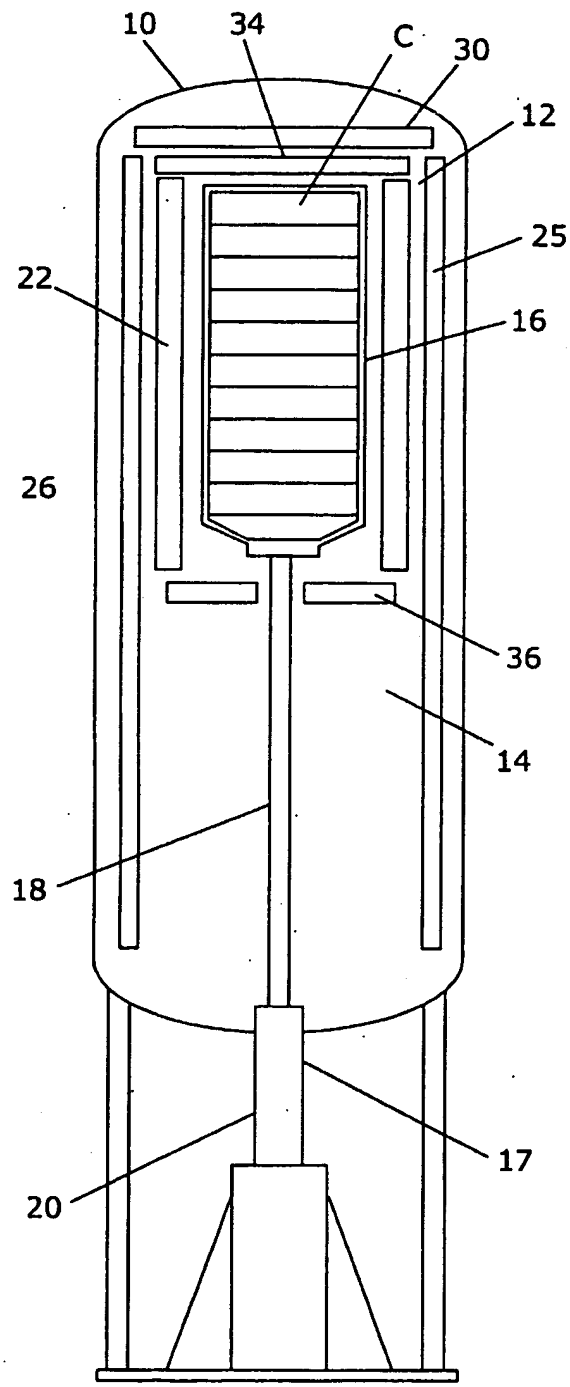

FIGURE 9B

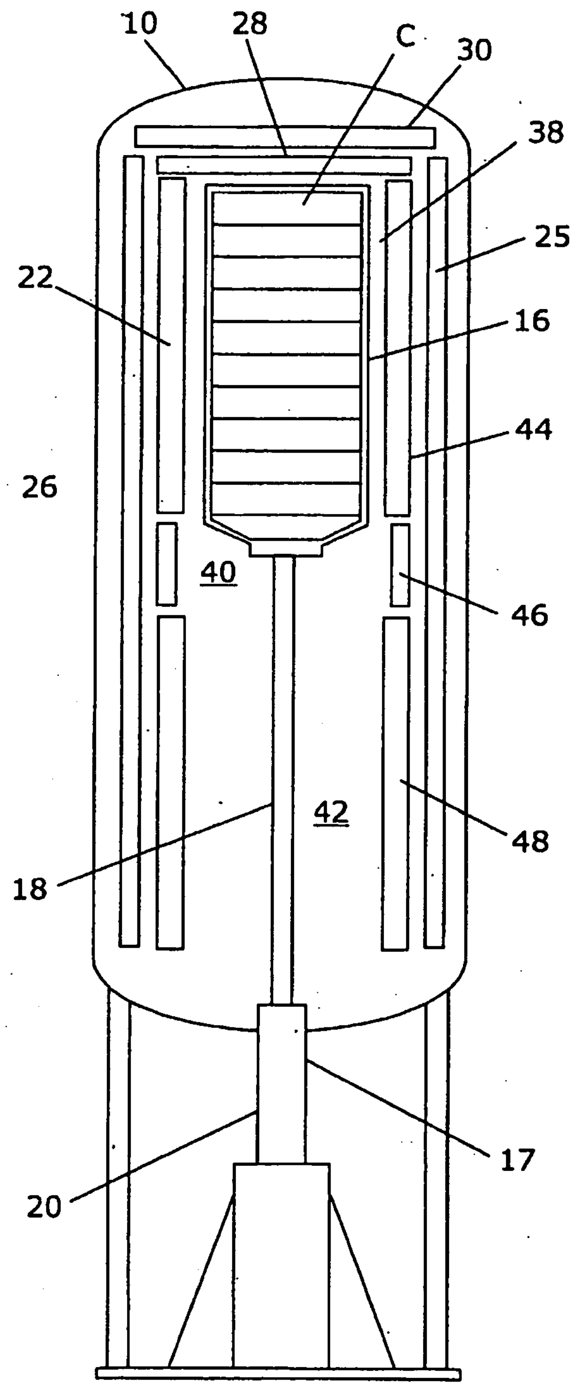

FIGURE 9C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/42467

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C30B 11/00, 15/06
US CL : 117/81, 83
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 117/81, 83

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
STN

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
HCAPLUS, JAPIO, INSPEC, USPATALL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,320,700 B2 (SHIOZAWA, et al) 20 November 2001, columns 2-15, lines 1-68, respectively	1-29

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date		
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 JANUARY 2002	23 JAN 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer FELISA HITESHEW Jean Proctor Paralegal Specialist Telephone No. (703) 308-0651

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